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High-temperature Exciton Superconductivity : Synthetic Aspects

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The present review examines for the first time the state of chemical synthetic studies directed towards the production of compounds and systems in which, in accordance with the proposed theoretical models, we may expect to realise the exciton mechanism of superconductivity and hence an increase in the critical temperature of the superconductivity transition. The bibliography contains 197 references.

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I. INTRODUCTION

The phenomenon of superconductivity is manifested in the disappearance of the electrical resistance of a substance when it is cooled below a definite so-called critical temperature (T_c). Superconductivity was first detected in mercury 60 years ago. It has now been established that most metals and several hundred alloys are superconductors[1].

The extensive utilisation of superconductors in technology is prevented by the fact that the critical temperatures of all known superconductors lie at very low temperatures. The highest value of T_c attained is $\sim 21°$ K [for the pseudo-binary compound Nb $(Al_{0.75}Ge_{0.25})$][2]. This is the first superconductor for which T_c lies above the boiling point of liquid hydrogen ($T_h = 20.3°$ K). All other superconductors have $T_c < 21°$ K (helium temperatures). Despite the large number of published papers, little progress have been made in this field: in the last 16 years, the maximal value of T_c has been raised by only 3 deg.

Theoretical calculations show that the critical temperatures of the known types of superconductor apparently cannot exceed 40° K.[3] This is related to the characteristic features of the phonon mechanism, which is responsible for superconductivity in metals, alloys, and a number of inorganic compounds.

At the present time, an extremely attractive approach to the production of high-temperature superconductors with $T_c \geqslant 80°$ K is provided by the preparation of compounds and systems in which it might be possible to realise a fundamentally different mechanism—the exciton mechanism—of superconductivity[3]. This mechanism and the related problem of the preparation of high-temperature superconductors has been discussed extremely intensively in recent years[3–5]. The extreme scientific and technical importance of the problem has been emphasised: in its possible importance for technology, the problem of the production of high-temperature superconductors takes second place only to the problem of producing controllable thermonuclear reactors[4, 6]. The possible existence of high-temperature superconductors has not yet been strictly proved theoretically, but it has not been refuted. Exciton superconductors have not been obtained even at low temperatures. Some authors have been extremely sceptical regarding the possibility of preparing high-temperature superconductors[2, 7], but the importance of the problem has recently been leading an increasing number of research workers to take up its experimental study.

The present review will deal chiefly with the state of chemical synthetic studies directed towards the production of compounds and systems in which, in accordance with the proposed theoretical models, we might expect to realise the exciton mechanism of superconductivity.

II. MECHANISMS OF SUPERCONDUCTIVITY

1. Phonon Mechanism

In 1957, Bardeen, Cooper, and Schrieffer[8, 9] developed the microscopic theory of superconductivity (the BCS theory). According to the BCS theory, the realisation of the superconducting state requires that two basic conditions be satisfied[5]. In the first place, between the conductivity electrons close to the Fermi surface there should be produced an attractive interaction exceeding their direct Coulombic repulsion. The attraction must be sufficiently strong for the formation of combined pairs of electrons. In the second place, all the pairs of electrons must be in the same quantum-mechanical state. Superconductivity is a collective effect: the pairing of two electrons takes place only when a large number of other pairs of electrons are in the same state.

The attraction between electrons in metals arises as a consequence of the interaction of the conductivity electrons with lattice vibrations—phonons. A "free" electron, moving through the ionic metallic lattice, attracts the positively charged metal ions and hence brings about deformation of the lattice close to itself. This leads to the appearance, in the lattice, of a region of excess positive charge, produced by the higher density of ions at the point where the lattice has been deformed. Since the ions move much more slowly than electrons, this region follows at a considerable distance behind the first electron. A second electron attracts the excess of positive charge, and hence interacts indirectly with the first electron

(attracting it). In other words, the interaction of the electrons with the positively charged ions creates vibrations in the lattice (phonons). The exchange of phonons between two electrons leads to their attraction to one another.

The binding energy of the paired electrons determines the critical temperature of the superconductivity transition. Theoretical estimates of T_c show that for the phonon mechanism of superconductivity, the critical temperatures apparently cannot exceed 40° K.[3] This conclusion is confirmed experimentally: in 60 years of research on superconductivity, all metals and a large number of metallic and semiconducting alloys have been studied, but values of $T_c > 21°$ K have not been detected. It should of course be noted that these theoretical estimates are somewhat arbitrary[3], since they are based on an examination of metals with known properties. The development of the technology of high and superhigh pressures has led to the possibility of creating new superconducting phases and compounds which are not formed under "ordinary" conditions[10]. Particularly promising in this connection is the production of metallic hydrogen[11], for which calculations give values of $T_c \sim 30-300°$K. In this connection, the preparation and study of heavy metal hydrides, which can be regarded as alloys based on metallic hydrogen, are of considerable interest[12]. It may be noted that superconductivity was recently detected in polyhydrides and polydeuterides of thorium (T_c = 8.05–8.35° K)[12].

2. Exciton Mechanism

In 1964, Little suggested the possibility of an electron-electron (exciton) mechanism of superconductivity[13–16], in which the attraction between the conductivity electrons arises not as a consequence of phonon exchange, but as a consequence of exciton exchange (electronic excitation). According to some estimates, the realisation of the exciton mechanism should lead to much higher values of T_c (~300° K or more)[14,15].

In contrast to the situation for the phonon mechanism, which is universal in character, the manifestation of the exciton mechanism of superconductivity requires a definite combination of two sub-systems, one conducting, and the other dielectric with a corresponding exciton spectrum. At the present time several models, in which an exciton mechanism may be established in principle, have been proposed[3].

III. MODELS OF ONE-DIMENSIONAL EXCITON SUPERCONDUCTORS

Little examined the chief characteristic features of the exciton mechanism of superconductivity and the possibility of its realisation for the example of a model organic macromolecule (Fig. 1)[5,13–16]. This macromolecule consists of a polyene chain, which plays the role of a one-dimensional metal or semiconductor, and readily polarised substituents, which ensure effective attraction between the conductivity electrons. The "free" electron of the conducting polyene chain ("core"), moving close to one of the substituents, polarises it in such a way that a positive charge is induced at the end of the substituent nearest the conducting chain. This charge attracts another electron of the "core", so that there is effective attraction of this electron to the electron which produced the initial polarisation of the substituent. The attraction may be greater than the direct Coulombic repulsion between the conducting electrons, so that the overall interaction between the electrons of the "core" will be an attraction, and this should bring the system into the superconducting state.

The idea of an exciton mechanism of superconductivity, and Little's quasi-one-dimensional model itself, attracted considerable attention and led to lively discussion[3–5,17–19].

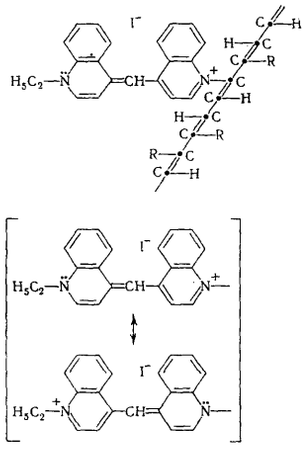


Figure 1. Little's hypothetical superconducting macromolecule.

The main objections are related to the one-dimensional nature of the model[5]. At the present time the question of which states can actually exist in the one-dimensional case with allowance for electron-electron and electron-phonon interactions is far from clear[18,20]. Thus Dzyaloshinskii and Larkin[20] have shown that, depending on the nature of the interaction between the electrons, a quasi-one-dimensional system may exist in different states: metallic, dielectric, antiferromagnetic, or superconducting.

One of the chief objections to Little's model is that in the one-dimensional system the fluctuations of electron density are large and should break down the superconducting state or at least lower T_c considerably. The fluctuations will be much smaller in fibrous structures[21], consisting of accumulations of conducting fibres in a three-dimensional non-conducting medium (the conductivity along the fibres being much greater than that in the perpendicular direction). In these structures, the advantages of the one-dimensional systems proposed by Little will be preserved, since the conducting fibre can be surrounded on all sides by molecules with appropriate electronic polarisability. The fluctuations of electron density, however, will in this instance be three-dimensional in character, and should not break down the superconducting state[4,21]. Structures of this kind are apparently more realistic for experimental realisation than Little's model.

IV. CHIEF REQUIREMENTS TO BE SATISFIED BY THE ELEMENTS OF LITTLE'S MODEL

It can be seen from Figs. 1 and 2 that Little's model consists of two interconnected parts: the quasi-one-dimensional conducting "core" and the readily polarised substituents. In principle, it is possible to use as "core" conjugated polymer chains of different types[16, 22–24]; chains of atoms[25, 26] of molecules [27–29] formed by appropriate arrangement of these units in a molecular crystal; quasi-metallic chains of iodine atoms[16]; etc. In its conducting properties, the "core" should be a metal or a semiconductor with a small gap[26]. For polymer systems, in Little's opinion, highly ordered stereoregular structures are not essential[26]. The length of the macromolecule may be of the order of 100 Å. Superconductivity in the entire specimen will possibly be produced as a consequence of the Josephson effect[26] (tunnelling of electron pairs between individual superconducting molecules through a non-superconducting phase[9]). The fundamental problem of the manifestation of superconductivity in a specimen consisting of superconducting macromolecules has not in fact been examined.

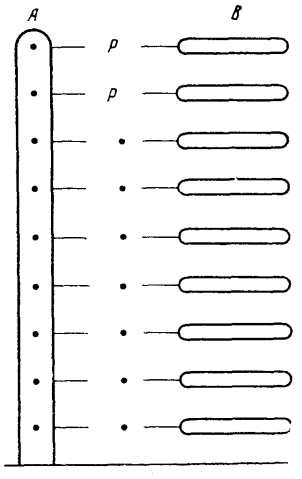


Figure 2. Model of a "one-dimensional exciton superconductor". A) Conducting "core", B) readily polarised substituents, P) connection between the elements of the model.

The substituents must satisfy certain requirements. They must be readily polarised, so that electronic excitations (excitons) which are not readily quenched can arise in them[3, 4]. This means that the substituents should have at least one low-lying excited level exhibiting a high dipole moment[17]. As substituents of this kind it is possible to use molecules (of the cyanine dye type) with a narrow absorption band in the region of ~ 1200 nm and an extinction coefficient of ~ 10^5.[18] It should, however, be noted that although dyes with intramolecular electronic transitions in the region of 1000 nm and above are known, they are generally sparingly soluble and insufficiently stable, so that it is extremely difficult to use them for preparative purposes. Other suggested possible substituents are nitroso-compounds, zwitter-ions, and dithiolene complexes of metals[30]. The latter have absorption bands in the near infrared range[31, 32]. In our opinion, it is also possible to use for the same purpose various organic and organometallic complexes of the semiconductor type, exhibiting a high polarisability (for example radical-ion salts of 7, 7, 8, 8-tetracyanoquinodimethane, and various complexes of iridium and platinum)[33, 34].

The problem of the spatial arrangement of the substituents in Little's model is important. For steric reasons, they cannot be placed on every carbon atom of the core. It is important, however, that the substituents be as close to one another as possible[16]. Moreover, the exciton system should be sufficiently close to the conducting core, since the effect of the induced charge decreases rapidly with separation[16]. There is however a limit to the distance between the polarised substituents and the conducting core, since at sufficiently small separations, exchange interaction between the conductivity electrons and the polarisation is possible, and this decreases the attraction between the conductivity electrons[16]. In Little's model, a decrease in exchange is achieved by having the lateral substituents arranged in a plane perpendicular to the core; there is then no conjugation between the core and the lateral substituents.

V. APPROACHES TO THE SYNTHESIS

At the present time there have been three general approaches to a synthesis based on Little's model. The first of these involves: 1) the creation of a one-dimensional conducting system (core); 2) the selection or synthesis of suitable readily polarised substituents; and 3) the synthetic combination of the two elements. This approach is not yet fully practical, even if only because linear conducting polymer chains are generally non-uniform and sparingly soluble. It is therefore unlikely that they could be subsequently used in a synthesis. In another approach, the aim is first to obtain a conducting chain containing relatively stable dye precursors, and then to convert these into the desired dyes. The third approach involves: 1) the synthesis of certain molecules containing readily polarised groups of substituents, and 2) the controlled polymerisation or crystallisation of these molecules.

We can now examine specific chemical approaches to the synthesis of Little's model. We shall also examine various types of quasi-one-dimensional systems which may prove to be suitable candidates for the role of the core in Little's model.

1. Polymers with a System of Conjugated Bonds

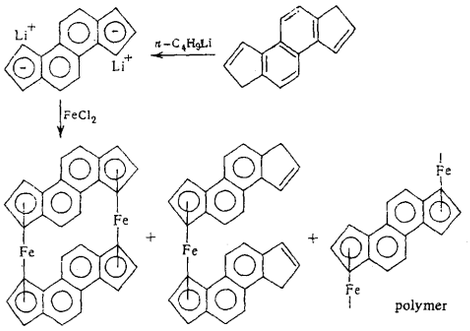
A large number of linear polymers with conjugated bonds, exhibiting semiconducting properties, have been described[35–38]. These properties are determined by two factors: the structure of the polymeric molecule (the system of conjugated π-bonds) and the supermolecular structure of the substance[37]. In most instances it is impossible to obtain polymers with a molecular weight $>$ 3000; the degree of polymerisation usually does not exceed 10.[37] The average extent of the effective intramolecular conjugation is usually less than the average degree of polymerisation, because the arrangement of the structural elements is frequently not coplanar[39]. Existing methods for the synthesis of polymers with conjugated bonds do not make it possible to obtain homogeneous

polymers with a given structure, a high molecular weight, and a narrow molecular-weight distribution. The problem of creating organic superconducting polymeric molecules probably requires fundamentally new approaches to the synthesis of polymers with conjugated bonds, which would make it possible to control closely the actual polymerisation process and to obtain conducting polymers with a rigorously defined structure.

We shall not examine in detail the various linear polymers with conjugated bonds, which formally can lay claim to the role of core in Little's model (polyacetylenes, polyynes, polyphenylenes, polyacenes). These polymers, in our opinion, are unsuitable for this purpose, since for the most part they have a high resistance ($\rho \simeq 10^5 - 10^{12}$ Ω.cm, $E \simeq 0.4-1.0$ eV)[38] and are amorphous, sparingly soluble, and somewhat unstable substances (particularly the polyacenes).

One of the most highly conducting linear polymers is polymeric sulphur nitride $(SN)_x$.[40] The polymer forms fibrous crystals with a metallic lustre, and is diamagnetic. Unfortunately, conductivity measurements have up to the present been carried out only with compressed tablets ($\rho_{0°C} \simeq 0.040-6$ Ω.cm, $E < 0.02$ eV)[40]. The study of the conducting properties of individual oriented fibres or crystals of polymeric sulphur nitride would be of considerable interest in view of its fairly high conductivity, which approaches that of metals.

Schneider[22] has discussed the advantages and disadvantages of various types of polymer with conjugated bonds, capable of laying claim to the role of core. In his opinion, alicyclic systems with a large number of possible degrees of freedom are undesirable, since in these compounds the maximal conjugation cannot be realised, because the polymer chain is insufficiently rigid. Aromatic cyclic systems exhibiting a high rigidity are suitable. Polyacenes are attracting attention in this connection, but these compounds have a low resistance to oxidation and low thermal and photochemical stability. Polyphenylenes are more stable, but in this instance loss of coplanarity is possible, and this influences the degree of conjugation. Another possibility is provided by metallocene polymers, in which polyconjugated groups are joined by metal atoms (Fig. 3). In an attempt to realise Little's model by synthesis, Schneider[22] prepared a metallocene polymer by the following scheme:



The main product was an insoluble amorphous polymer with high molecular weight. Because of its extremely low solubility, it could not be purified and was not well characterised. The disadvantages of this approach are immediately apparent: a conducting polymer core can probably be obtained in this way, but it is difficult to characterise and, which is more important, it is not clear how readily polarised substituents can be attached to it.

Another type of polymer is exemplified by polychelates, in which the metal atom is in the main polymer chain, forming a chelate unit in the conjugation chain.

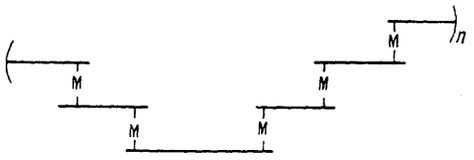


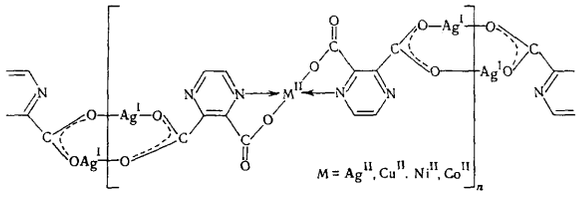
Figure 3. Polymeric metallocene: alternating planar aromatic hydrocarbon rings and metal atoms.

Dewar and Talati[41, 42] suggested that it is possible to prepare chelate polymers with a high conductivity from a suitable transition metal and an aromatic ligand capable of binding two metal atoms. To create conjugation in this system, each metal must form $d\pi - p\pi$ bonds with two neighbouring ligands, using the same d orbital. The conditions are satisfied if the ligands are coplanar and are situated in the *trans*-position relative to one another in an octahedral or square-planar complex. On this basis, the authors cited prepared polymeric chelate complexes of Cu^{II}, Ni^{II}, and Pd^{II} with 1,5-diformyl- and 1,5-diacetyl- 2,6-dihydroxynaphthalene dioximes[41, 42]. Some of the complexes obtained showed a relatively high conductivity ($\sim 10^{-4} - 10^{-5}$ Ω^{-1} cm^{-1}, $E = 0.23$ eV). The molecular weights of the polymers were low, and their degree of polymerisation did not exceed 10. Polymeric complexes of analogous type were also prepared by Kanda and Kawaguchi[43].

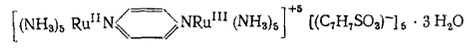
Electron transfer in these systems can probably be intensified by introducing suitable metals in different oxidation states into the chain. In particular, Bolto and Weiss[44] suggested that the higher conductivity of the Fe-containing polymer compared with the polymers of other metals obtained by the reaction of chloranil with *o*-phenylenediamine in the presence of the metal salts is due to the presence of two different oxidation states of iron in this polymer.

It may be noted that a large number of inorganic compounds containing ions of the same element in different oxidation states are now known[45, 46]. Many of these mixed-valency compounds exhibit characteristic chemical and physical properties (colour, magnetism, conductivity, and reactivity). Thus the metal–metal distances in the crystal lattices of Fe_2O_3 and Fe_3O_4 are almost the same (3 Å), but the conductivity of Fe_3O_4 (a compound with mixed valencies Fe^{II} and Fe^{III}) is greater by six orders of magnitude than that of Fe_2O_3.[47] The high conductivity (2.5×10^2 Ω^{-1} cm^{-1}) of Fe_3O_4 is attributed to rapid valency charge exchanges between iron atoms in different oxidation states[48].

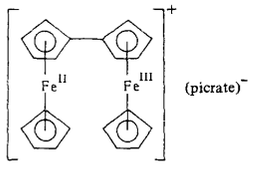
Chelate polymers containing metal ions in different oxidation states were recently prepared[49, 50]. Pyrazine-2, 3-dicarboxylic acid was used as model ligand:



Study of these polymeric complexes by static magnetic susceptibility and NMR methods at helium temperatures showed, however, that the unpaired electrons of the paramagnetic metals interact weakly with one another[51]. The probable reason is that in these complexes the conjugation chain is broken at the ends of the individual fragments. Despite this result, chelate polymers containing ligands with conjugated chains and metal ions in different oxidation states are extremely promising materials for the preparation of highly conducting linear compounds. In fact, in complexes of the type M–L–M′, where M and M′ are ions of the same element in different oxidation states, and L is a ligand with conjugated bonds, it has been possible to detect electron transfer between the metal ions. Creutz and Taube[52] made this observation for the ruthenium complex:

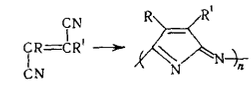


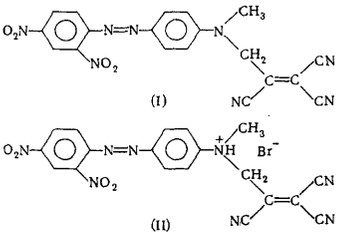
Analogous electron transfer between iron atoms in different oxidation states was observed by Kaufman and Cowan[47] in bis (ferrocinium) picrate:



The conductivity of the latter was greater by 5–6 orders of magnitude than that of ferrocene or ferrocinium picrate. Also noteworthy is the existence of electrically conducting complexes containing linear chains of metal ions with different valencies, joined by bridging groups[53] (Cl, Br) (for example, $Pd^{II}(NH_3)_2.Cl_2Pd^{IV}(NH_3)_2Cl_4$). Some of these complexes exhibit anisotropic conductivity, the greatest conductivity being observed along the linear M^{II}–Cl–M^{IV} chains.

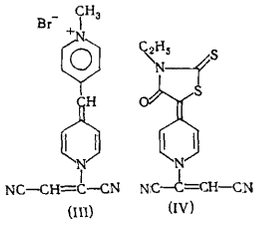
An interesting attempt to obtain possible superconductors was made by Liepins and coworkers[23], who prepared nitrile monomers (I–IV) containing dyes as substituents, and then carried out the polymerisation of these monomers at the nitrile groups:





(I)

(II)

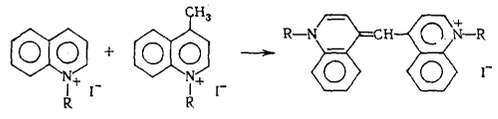


(III)

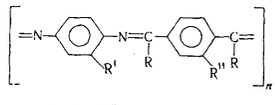
(IV)

The polymers obtained had a low conductivity ($\sim 10^{-8} - 10^{-12}\ \Omega^{-1}\ cm^{-1}$), however, and superconductivity was not detected. These polymers are apparently non-uniform and disordered; their structure is not known exactly. This is the chief disadvantage of the "polymer" approach: it is impossible to obtain conjugated polymers with a strictly defined structure.

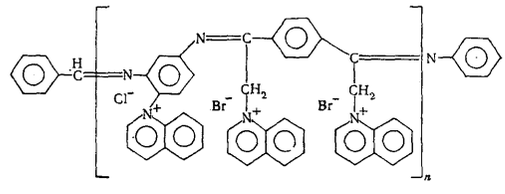
Hodgkin and Heller[24] suggested the initial preparation of a conjugated polymer chain containing relatively stable dye precursors, followed by their conversion into the desired dyes. Cyanine dyes were chosen, since they are readily obtained by the reaction of two quaternary heterocyclic bases, one of which contains an active methyl group:



Thus the first stage of the problem reduced to the preparation of polymers with a system of conjugated bonds, having as substituents quaternary heterocyclic bases, in particular quinoline bases. Polymers based on aromatic Schiff's bases were selected. The aim of the work was primarily to prepare polymers with a high molecular weight and the introduction of substituents to increase the degree of conjugation. The authors cited prepared a number of model Schiff's bases and their polymers, including a polymer containing quaternary quinoline nuclei as substituents:



(R, R′, R″ = H or dye)



In this polymer, one of the quinoline nuclei is joined directly to the aromatic ring, and this is undesirable, since exchange is then possible between the conducting system and the readily polarised system. Subsequently, Hodgkin and Heller proposed the preparation of monomers in which the quaternary quinoline nuclei are separated from the aromatic rings of the main conjugation chain by a methylene group[24]. An analogous approach has been used for the preparation of polymeric polymethine dyes[54].

In the systems examined above, the conducting core is polymeric; we shall now describe compounds in which the conducting chains are formed from atoms or molecules as a consequence of their appropriate arrangement in a molecular crystal. In our opinion, these compounds exhibit definite advantages over polymers, since they can be obtained in the form of single crystals and with a high degree of purity.

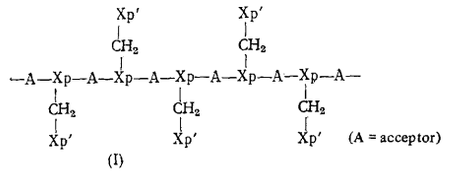
2. Charge-transfer Complexes

Charge-transfer complexes (CTC) are extremely varied[55–57], and many exhibit semiconducting properties[35, 36]. A characteristic feature of the structure of electrically

conducting CTC is the presence, in the crystal, of stacks consisting of alternating molecules of a donor and an acceptor, the distances between which are usually slightly less than the normal van der Waals' distances[35, 36, 58–61]. Thus in the ferrocene–tetracyanoethylene (TCE) complex the distance between the parallel planes of the TCE molecules and the cyclopentadienyl rings is 3.14 ± 0.1 Å[61]. The "stack" structure of the CTC should lead to anisotropy of the electrical conductivity of their single crystals, and this has been observed experimentally[62, 63]. For example, the maximal value of the conductivity ($\sigma = 10^{-5}\ \Omega^{-1}\,cm^{-1}$, $E = 0.23$ eV) in single crystals of the complex of perylene with bis [1, 2-di (trifluoromethyl) ethylene-1, 2-dithiolato]-nickel is observed along stacks consisting of alternating molecules of perylene and the complex acceptor[63].

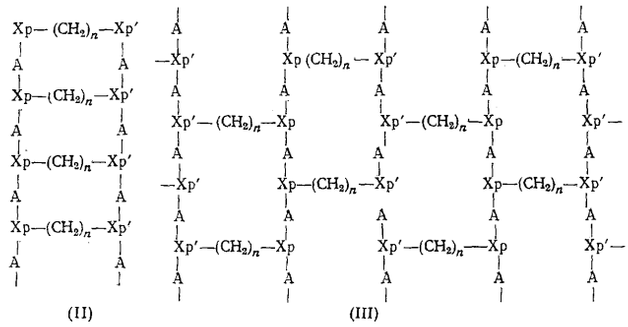
The ability of CTC to form electrically conducting stacks of alternating molecules of a donor and an acceptor in a crystal can apparently be used as a basis for the preparation of various compounds which are models of Little's molecule.

It is to be expected, for example, that in CTC containing bis-dyes with isolated chromophores as the donor component[14], one chromophoric system (Xp) will take part in the formation of the CTC, forming the electrically conducting stack in the crystal, while the other (Xp′) will act as the readily polarised substituent (structure of type I):



(I)

Since the chromophores are isolated, electron exchange between the conducting and polarised electrons in this system is unlikely; at the same time, exciton interaction is possible between two electronic systems at distances of the order of 3 Å. When bis-dyes with bridges longer than –CH_2– between the chromophores are used, other types of structure (II and III) are not excluded:

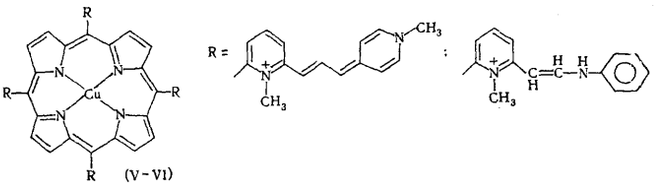


For bis-dyes with one CH_2 bridge, CTC structures of types (II) and (III) are unlikely, because of the steric hindrance created by the acceptor molecules. Structure (II) is of interest, since of the two stacks connected to one another, one can be regarded as conducting, and the other as polarised. As analogous situation is observed in the double spiral of DNA. In the opinion of some authors[65, 66], the production of increased conductivity of the superconductivity type is possible in certain regions of one DNA spiral as a consequence of the excitation of electrons of another spiral.

The network structure (III) consists of conducting filaments (stacks) joined to one another; the conductivity along the filaments is greater than that in the perpendicular direction (fibrous structures)[21].

The chief difficulties are apparently associated with the preparation of highly conducting donor-acceptor stacks and the production of a structural correspondence between the components of the CTC. Very few charge-transfer complexes based on dyes have yet been described[67, 68], and almost no studies have been made of the conducting properties of this type of CTC.

The preparation of CTC using not bis-dyes but porphyrin molecules (V–VI) containing dyes as substituents[69] is of interest:



(V-VI)

Porphyrin CTCs, in particular with nitro-compounds as acceptors, have been described[70, 71]. Complexes of etioporphyrin and its copper and nickel derivatives with 7, 7, 8, 8-tetracyanoquinodimethane (TCQM) were recently prepared[25]. The use of porphyrin molecules (V, VI) as CTC components is of particular interest, since exciton interaction between the electronic systems of the dyes and the porphyrin has apparently been detected in these complexes[69]. The position of the so-called Soret band in the absorption spectra of porphyrins usually remains unchanged when electron-accepting or electron-donating substituents are introduced into the ring at the methine bridge. In the spectra of compounds (V, VI), however, the Soret band was displaced appreciably towards longer wavelengths[69]. These shifts were attributed to exciton interaction between the electronic systems of the dye and the porphyrin ring: an electron in the ring generates an exciton in the dye, which can then interact with another electron of the ring. This should lead to a decrease or increase in the Coulombic repulsion between the electrons of the porphyrin ring, and hence to a change in the position of the energy levels in the molecule. The experimentally determined directions and magnitudes of the shifts corresponded to the calculated values[69].

3. Radical-ion Salts

Radical-ion salts represent a limiting case among CTC, where complete separation of the charges between the components of the complexes takes place even in the ground state[35, 55–57].

A characteristic feature of the crystal structure of a number of radical-ion salts is the presence, in the crystal, of stacks consisting of only radical-cations in the case of radical-cation salts[72–74] or only radical-anions in the case of radical-anion salts[75–84]. In contrast to the situation for a CTC, the stacks are formed in this instance from the same molecules (radical-ions of a given sign), the distances between which are usually slightly shorter than the normal van der Waals' distances. Strong interactions may arise within the stacks, and these are responsible, in particular, for the conductivity[85, 86], magnetic properties[86–90], and spectroscopic properties[91–95] of compounds of this type. In those instances where both components of the radical-ion salts are paramagnetic, the stacks

usually consist of alternating radical-cations and radical-anions[96–98].

Information is now available on a number of conducting radical-ion salts, based on strong π-donors: tetrathiotetracene[99], dibenzophenothiazine[100], and derivatives of N,N′-diphenyl-p-phenylenediamine[101], or based on strong π-acceptors: 7,7,8,8-tetracyanoquinodimethane (TCQM)[102], 11,11,12,12-tetracyano-2,6-naphthoquinodimethane[103], 9-dicyanomethylenepolynitrofluorenes[104], etc.[105]. Many of these compounds have a fairly high conductivity ($\sigma \geqslant 10^{-2}\ \Omega^{-1}\ cm^{-1}$, $E \leqslant 0.1$ eV). Radical-ion salts based on TCQM have attracted particular attention[85, 86, 106–114]. Organic salts of TCQM include compounds for which the conductivity approaches that of metals ($\sigma = 10^{2}\ \Omega^{-1}\ cm^{-1}$, $E = 0.02–0.05$ eV)[85, 86].

7,7,8,8-Tetracyanoquinodimethane forms three types of conducting compound: π-complexes and simple and complex radical-ion salts[102]. TCQM forms π-complexes (charge-transfer complexes) with aromatic hydrocarbons, amines, phenols, and various other compounds. These compounds are for the most part poor conductors[102]. ($\rho = 10^{7} - 10^{10}\ \Omega.cm$), and their crystal structure is the same as that of most CTC: it consists of stacks formed by alternating molecules of a donor and an acceptor[58]. The second type of compound formed by TCQM consists of simple radical-anion salts with the general formula $K^{+}(TCQM)^{\cdot}$, where K^{+} may be a metallic, organometallic, or organic cation.

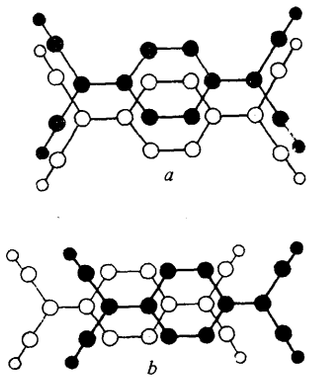


Figure 4. Two basic types of overlap between molecules of TCQM and its salts.

Most simple salts have a relatively high resistance[102] ($10^{4} - 10^{11}\ \Omega.cm$), but they also include some good conductors ($\sigma \leqslant 10^{-1}\ \Omega^{-1}\ cm^{-1}$)[85, 108, 113, 115].

X-ray diffraction study[78, 80, 84] of the salt [bis (toluene) chromium]$^{+}(TCQM)^{\cdot}$ ($\rho = 3.5 \times 10^{8}\ \Omega.cm$)[110] showed that the TCQM radical-anions form stacks within which it is possible to distinguish pairs formed by TCQM molecules with an interplanar spacing equal to 3.37 Å. The distance between the pairs is 3.43 Å. The overlap of two neighbouring TCQM molecules in the stack is of type a in Fig. 4. The conductivity of this salt along the direction of the stacks is about two orders of magnitude greater than that of a compressed tablet. The TCQM spin system is here diamagnetic[88] at room temperature, indicating strong magnetic interaction in the $TCQM^{\cdot}$ chain (paired interaction).

In general, most poorly conducting simple salts of TCQM containing diamagnetic cations either are diamagnetic at room temperature or exhibit weak paramagnetism, which increases with increase in temperature (singlet-triplet behaviour)[87]. It should be noted that stacks are not always present in crystals of simple salts of TCQM[84, 116]. In those instances where they are not formed, the radical-anions are still arranged in individual pairs[84, 116].

The tendency for TCQM radical-anions to undergo dimerisation both in the solid state and in solution[117] is apparently a fairly general property of organic radical-ions[118]. An interesting feature is that the organometallic radical-anions of the chelate dithiolene complexes of metals also form stacks in crystals of salts with organic cations. Pairs of these radical-anions can be distinguished within the stacks[119]. The magnetic behaviour of these salts is effectively described by paired interaction[119].

The TCQM salts examined above are the poorly conducting simple salts, but, as we have already noted, some simple salts of TCQM are good conductors. Thus (N-methylphenazinium)$^{+}(TCQM)^{\cdot}$ is one of the most strongly conducting organic compounds ($\sigma \simeq 10^{2}\ \Omega^{-1}\ cm^{-1}$)[86, 108, 113]; this salt is similar to the conducting complexes of TCQM[86].

Complex salts with the general formula $K^{+}(TCQM)^{\cdot}(TCQM)$ form the most interesting type of conducting compounds of TCQM. In addition to the TCQM radical-anion, they contain the formally neutral TCQM molecule[102]. K^{+} may be an organic or organometallic cation (metal cations, with the exception of Cs^{+}, do not form complex salts)[102]. A characteristic feature of these TCQM salts is their conductivity, which is unusually high for organic compounds ($10^{2} - 10^{3}\ \Omega^{-1}\ cm^{-1}$)[102].

The complex salts can be regarded as compounds of TCQM with mixed valency (-1 and 0), in which one electron is delocalised over two TCQM molecules $[(TCQM)_{2}^{-}]$.

The ability of the TCQM radical-anion to form complex salts is not apparently a specific property of TCQM molecules alone. Complex salts based on other radical-anions are now known[103, 105].

A characteristic feature of the crystal structure of most complex salts of TCQM is the presence, in the crystal, of stacks consisting of TCQM molecules arranged one above the other, with a slight displacement[76, 77, 79–84]. The conductivity of the salts is generally strongly anisotropic and has a maximal value along the direction of the stacks[85, 86]. The dimensions and geometry of the cation have a significant influence on the mutual arrangement of the TCQM molecules in the stack and on the distance between them, and hence on the conductivity and magnetic properties of the salts[120]. The highest conductivity ($\sigma \simeq 10 - 100\ \Omega^{-1}\ cm^{-1}$, $E = 0.025 - 0.050$ eV)[85, 86, 114] is shown by complex salts of TCQM, containing as cations planar aromatic heterocyclic bases with H- or CH_3- (but not $-C_2H_5$) substituents attached to the nitrogen atom[106, 107]. The paramagnetic susceptibility of the highly conducting salts of TCQM depends little on temperature in the range above 30°K[86, 87].

In the crystals of these salts, the distances between the TCQM molecules in the stack are equalised, and are much shorter than the normal van der Waals' distances, and the TCQM molecules overlap one another in characteristic fashion: the centre of one molecule is

situated above the centre of the double quinodimethane bond of another molecule[75, 79, 82, 84] (overlap of type *b* in Fig. 4). Thus in the complex salt (quinolinium)$^+$-(TCQM)$_2^-$, which is one of the most strongly conducting organic compounds (σ = 100 Ω^{-1} cm^{-1}, E = 0.03 eV)[85, 86, 114], the TCQM molecules are equivalent (each can be assigned a charge of $-\frac{1}{2}$), the interplanar spacings in the stack are equal (3.22 Å)[82], and the overlap is of type *b*. Analogous packing of the TCQM molecules is observed in the stacks in the complex salt [bis(toluene)chromium]$^+$(TCQM)$_2^-$ (Fig. 5)[79, 80], but the distance between the TCQM molecules is here greater than 3.29 Å, and the molecules are crystallographically non-equivalent. The conductivity of this salt is lower by almost two orders of magnitude than that of (quinolinium)$^+$(TCQM)$_2^-$ [110]. On going from the simple salt of bis(toluene) chromium to the complex salt, the interplanar spacings in the stack are equalised, and become slightly shorter; at the same time there is a change in the nature of the overlap, which becomes more effective. The conductivity increases by five orders of magnitude, and the activation energy decreases by a factor of four[110]. Packing analogous to that in (quinolinium)$^+$(TCQM)$_2^-$ is shown by the highly conducting simple salt (N-methylphenazinium)$^+$(TCQM)$^-$ [75], and also by (N, N, N′, N′-tetramethyl-*p*-phenylenediamine)$^+$ - (TCQM)$_2^-$ [77]. The conducting properties of the last compound have not yet been studied, but it may be assumed that the compound has a high conductivity.

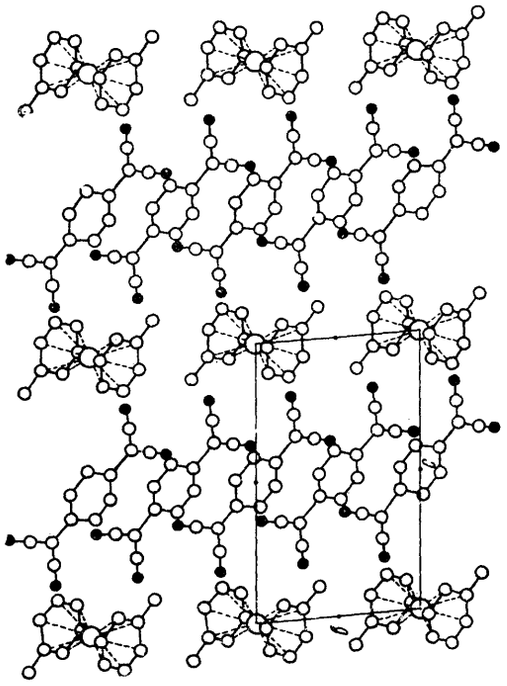


Figure 5. Projection of the structure of the complex salt [bis (toluene) chromium]$^+$ (TCQM)$_2^-$ on the [100] plane [79, 80].

Unlike the complex salts of TCQM with heterocyclic bases containing H- or CH_3-substituents attached to the nitrogen atom, complex salts of TCQM in which the cations are formed by metals, aliphatic bases, or various other non-planar systems generally exhibit a lower conductivity[85, 86], and their paramagnetism is singlet-triplet in character[86, 87, 121]. In these complex salts there is an alternation of spacings between the TCQM molecules in the stack, and these molecules in the stack form structurally repeating groups of two[84, 122, 123], three[76], or four[81, 83]; there is strong overlap within the pairs, but there may be no overlap at all between the pairs[122, 123].

The ability of the TCQM radical-anion to form quasi-one-dimensional conducting stacks in crystals can be used to prepare compounds which provide models of Little's molecule. In 1967, Khidekel' and coworkers[27, 28] and Lupinskii and coworkers[29] suggested that the radical-ion salts of TCQM with dyes may exhibit superconducting properties, since they formally satisfy the necessary conditions for the production of superconductivity: the presence of a linear conducting system (stacks of TCQM molecules) and readily polarised groups (dye cations). The compounds prepared, however, did not exhibit superconducting properties[27–29, 114], although some of them had a high conductivity ($\rho \simeq 10$ Ω. cm, $E \simeq 0.04-0.05$ eV)[27, 28, 124]. The problem of why the compounds obtained do not exhibit superconducting properties is extremely complex: here we shall restrict ourselves to an examination of some possible factors. In the first place, the dyes used[27–29, 124] are not highly polarisable ($\lambda \simeq 500-600$ nm). According to the latest calculations[16], it is necessary to have dyes with absorption bands in the region of 1200 nm. Unfortunately, complex salts of TCQM with cyanine dyes, which absorb light in the region of 700 nm and above, cannot be prepared. This is due to the fact that with increase in the length of the conjugation chain there is an increase in the basic nature of the dye, that is in its ability to undergo oxidation, so that these dyes are oxidised in their reaction with TCQM.

In contrast to Little's model, in which the bond between the conducting chain and the dye is covalent, with length ~ 1.5 Å, the bond in the compounds being considered is predominantly ionic, with length greater than 3 Å. It should however be noted that distances of the order of 3 Å may not be a significant obstacle for exciton interaction. A cardinal problem is the mechanism of conductivity in the highly conducting ($\sigma = 10^1-10^2\ \Omega^{-1}$ cm^{-1}) radical-ion salts of TCQM. If these compounds exhibited conductivity of the metallic type, as suggested earlier[85], they would be almost ideal starting materials for the preparation of organic superconductors. Recent studies[33, 86, 113, 114] of the conducting properties of single crystals of these complexes over a wide range of temperature (4 – 300° K), however, showed that these compounds are semiconductors with a low conductivity activation energy (0.022–0.05 eV) in the range below 200 – 150° K (there is no activation energy of conductivity in the region of room temperature) (Fig. 6). In these compounds the conductivity apparently involves a jump mechanism[86, 114], and not a zone mechanism, that is there is a system of localised current carriers, the movement of which at each stage must necessarily include a thermally activated jump. It should however be noted that in the opinion of some authors[125], the simple salt (N-methylphenazinium)$^+$(TCQM)$^-$ is a "metal", which at temperatures below 200° K is gradually converted into a semiconductor. The problem of the mechanism of conductivity is fundamental, since in a system of localised current carriers the transition to the superconducting state is impossible.

On the whole, the class of compounds based on TCQM and its analogues are extremely interesting materials for

further study. There exist considerable synthetic possibilities for the preparation of new radical-ion salts. Of the greatest interest are TCQM salts containing cations with a high polarisability. Highly conducting complexes of TCQM with tetrathiotetracene (TTT) have now been prepared[126]. The TTT radical-cation introduced into the complexes has absorption bands in the near infrared range (λ = 1000–1300 nm)[99]. The compounds obtained are also of interest in connection with the fact that each of the ionic components of the complex is individually capable of forming highly conducting radical salts.

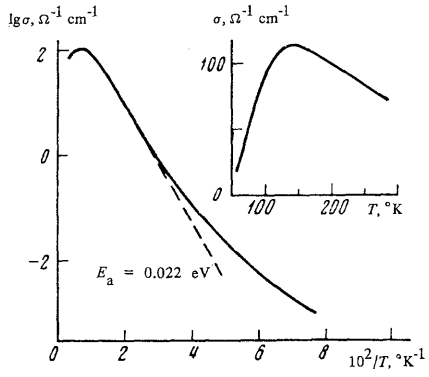


Figure 6. Temperature dependence of the conductivity of single crystals of the complex salt (acridinium)$^+$ (TCQM)$_2^-$ (constant current). The dependence is typical of that for highly conducting ($\sigma_{293°K} \sim 10^2\ \Omega^{-1}\text{cm}^{-1}$) TCQM salts.

An increase in the exciton interaction between the stacks of cations and the stacks of radical-anions in TCQM salts can apparently be achieved by the introduction, for example into the cation, of substituents capable of forming hydrogen bonds[127].

It is also not excluded that with the appropriate choice of cation it will be possible to prepare conducting stacks of TCQM with distances of less than 3.22 Å between the planes of the TCQM molecules (the distance of 3.20 Å is apparently not limiting: shorter intermolecular distances are known, for example 3.10 Å[72]). A decrease in the distances should lead to even stronger exchange interaction between the TCQM molecules in the stacks, and hence possibly to new effects related to the electrical and magnetic properties of these compounds (possibly the production of actual metallic conductivity). The production of an "organic metal" would be a great step forward on the road to the production of organic superconductors (this is particularly interesting in that the question of the possibility that a one-dimensional metal can exist has not yet been finally resolved). Moreover, organic compounds exhibiting a high conductivity may reveal new and previously unknown properties. In this connection, mention may be made of an unusual property detected in highly conducting radical-ion salts of TCQM: the anomalously high value of the dielectric constant (ϵ) at a frequency of 10^{10} Hz at low temperatures [for (acridinium)$^+$(TCQM)$_2^-$, $\epsilon_{4.2°K}$ = 800 ± 100, and for (N-methylphenazinium)$^+$ (TCQM)$^-$, $\epsilon_{4.2°K}$ = 350 ± 50], so that these compounds can be called superdielectrics[33].

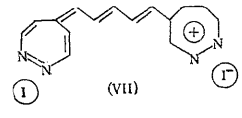
4. Poly-iodine Chains

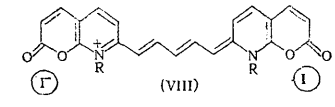
Linear chains of iodine atoms provide another possibility for the production of a conducting core[16]. It is well known that iodine can react with starch and other polysaccharides to form coloured complexes (so-called inclusion compounds)[128]. The macromolecules of amylose (a component of starch) apparently have a structure consisting of a screw or spiral with approximately six glycoside residues in each loop. Inside this loop there is a vacant cavity (or channel) with diameter 5 Å, into which the iodine is introduced. The iodine atoms are arranged linearly inside the amylose spiral with an interatomic distance of 3.1 Å[126]; all the I–I bonds are equalised[126]. In the opinion of some authors, this poly-iodine chain can be regarded as a quasi-one-dimensional metal[16, 128, 129]. The amylose–triiodide complex has been found to give an EPR signal assigned to Pauli paramagnetism, characteristic of metals[129] but these observations were subsequently not confirmed[130].

The question of the possible existence of the metallic state in poly-iodine chains is very important in connection with the problem of exciton superconductivity. To answer this question it would be necessary to study the electrical and magnetic properties of these compounds over a wide range of temperatures.

Although the metallic state has not been observed experimentally in poly-iodides, the semiconducting properties of poly-iodine compounds are familiar[131]. A complex of iodine with pyridazine, with a high conductivity ($\rho \leqslant 50\ \Omega$. cm, $E \leqslant 0.15$ eV) was recently described[132]. The study of the highly conducting ($\sigma = 3.4 \times 10^{-1}\ \Omega^{-1}\ \text{cm}^{-1}$, E = 0.07 eV) complex of iodine with N,N′-diphenyl-p-phenylenediamine showed that the electronic conductivity of this complex in the range between +50° and −50° is determined by the poly-iodine chains, in which the distances between the iodine atoms are non-equivalent: 2.99 Å and 3.77 Å[133].

Iodine can form inclusion compounds not only with polysaccharides, but also with other macromolecules: nylon, polyvinyl alcohol, and polyvinyl borate[128]. X-ray diffraction study of the polyvinyl alcohol–iodine complex showed poly-iodine chains with I–I distance equal to 3.1 Å[128]. Many relatively simple organic molecules also form complexes of this kind with iodine. Thus the compounds formed by iodine with diphenylpyrone and coumarin contain linear chains of iodine atoms with I–I distance equal to 3.06 Å[128]. For the diphenylpyrone complex it is suggested that the iodine is situated between the four phenyl groups of two pyrone molecules. These iodine atoms form a chain in the crystal[16]. A similar structure was recently proposed for the complex of bis (diphenylglyoximato) palladium(II) with iodine[134]. In Little's opinion, exciton interaction between the conductivity electrons and the polarisation electrons is possible in iodine complexes of this type, and this should lead to attraction between the conductivity electrons of the quasi-metallic poly-iodine chain, and hence to conversion of the system into the superconducting state[16]. Kagan[135] recently suggested the possibility of preparing superconductors from the starting materials (VII) and (VIII):





These compounds are extremely interesting, since they combine a high polarisability with the ability to stabilise quasimetallic poly-iodine chains.

5. Chains of Metal Ions

A number of complex compounds contain linear chains of metal ions[136–144]. Some of these compounds exhibit a high conductivity ($\sim 10^2\ \Omega^{-1}\ cm^{-1}$) along the metallic chain[34, 145–147]. A number of authors have therefore suggested that the polyene core in Little's model be replaced by a system of stacks of metal ions[25, 148–150].

Electrically conducting organometallic complexes containing chains of directly interacting metal ions can be divided into two groups: 1) complexes in which all the metal ions in the linear chain are in the same oxidation state[151–159] (Table 1), and 2) complexes containing metal ions in a linear chain in formally different oxidation states[34, 86, 145–147, 160–162].

Table 1. Electrical conductivity (σ), activation energy (E), and metal–metal distance in various complexes containing linear chains of metal ions in the same oxidation state.

Complexes	M–M distance, Å	Refs.	Conductivity, $\Omega^{-1}\ cm^{-1}$: single crystal $\sigma_{\parallel}$ (25°C)	single crystal $\sigma_{\perp}$ (25°)	powder σ_{tablet} (25°C)	$E_{\parallel}$[a], eV	References (conductivity data)
Ni(DMG)$_2$[b]	3.245	136	$1.01\cdot10^{-10}$	—	10^{-15}	0.57	157
Pd(DMG)$_2$[b]	3.26	136	$3.3\cdot10^{-10}$	—	10^{-15}	—	
Pt(DMG)$_2$[b]	3.23	138	10^{-12}	—	10^{-15}	—	
Ir(CO)$_2$ (acac)[c]	3.23	151, 152	10^{-5}	$2\cdot10^{-8}$ [d]	—	0.27	151, 152
Rh(CO)$_2$ (acac)[c]	3.26	141	10^{-11}	10^{-13} [e]	—	0.44	151, 152
Rh(CO)$_2$ (8-oxq)[f]	3.1	142	—	—	—	—	
[Pt(NH$_3$)$_4$] [PtCl$_4$]	3.23	137	$4.54\cdot10^{-4}$	$2\cdot10^{-6}$	$2.0\cdot10^{-8}$	0.3	157
[Pd(NH$_3$)$_4$] [PtCl$_4$]	3.25	139	$2.4\cdot10^{-8}$	—	—	—	157
[Pt(NH$_3$)$_4$] [PdCl$_4$]	3.225	140	$5.0\cdot10^{-9}$	—	—	—	157
K$_2$[PtCl$_4$]	4.13	157	$4\cdot10^{-12}$	$2\cdot10^{-12}$	10^{-14}		157
Sr[Pt(CN)$_4$]3H$_2$O	3.09	144	—	—	—	—	—
Be[Pt(CN)$_4$]2H$_2$O	3.16	144	—	—	—	—	—

[a] Activation energy of the conductivity generally isotropic[152, 156]; [b] (dimethylglyoximate)$^-$; [c] (acetylacetonate)$^-$; [d] $\sigma_{\parallel} : \sigma_{\perp} > 500$; [e] $\sigma_{\parallel} : \sigma_{\perp} > 100$; [f] (8-quinolinolate)$^-$.

Complexes of the first group (with square-planar structure) (Table 1) have a characteristic crystal structure[136, 138, 171, 142, 151, 152, 157]: the molecules are arranged one above the other, forming chains of metal ions along the C axis of the crystal with a relatively short metal–metal distance (3.1–3.4 Å). In Magnus' salt $[Pt(NH_3)_4]^{2+}[PtCl_4]^{2-}$ and its analogues, the stacks consist of alternating planar anions and cations[137, 139, 140]. In salts of the $K_2[Pt(CN)_4]$ type, the stacks are made up of identical anions[144].

Complexes of this type exhibit anisotropy of their conductivity (Table 1), the conductivity being a maximum along the chain of metal ions ($\sigma_{\parallel}$). The mechanism of conductivity in Magnus' salt, and also in the dicarbonylacetylacetonato-compounds of Ir^I and Rh^I has been treated by a number of authors within the framework of the zone theories[152, 157, 159], as follows. The d_{z^2} orbitals of the metal atoms overlap and form a valency zone[139], which in square planar complexes of metals with the d^8 electronic configuration is completely filled. The valency zone is separated by a large gap (ΔE) from the conductivity zone formed by the overlapping p_z orbitals; the doubled value of the activation energy for conduction corresponds to the magnitude of the gap between the valency zone and the conductivity zone. For Magnus' salt, ΔE = 0.6 eV (4840 cm^{-1})[157]. The absorption spectrum[139, 163] of the complex along the *c* axis shows a band with a maximum of 6400 cm^{-1} (the start of the absorption lies at 4500 cm^{-1}), which is close to the magnitude of the energy gap obtained from the temperature dependence of the conductivity. Moreover, Magnus' salt shows photoconductivity with a threshold at 4500 cm^{-1}.[152]. All this provides evidence in support of the zone mechanism, but the overall problem of the mechanism of conductivity in these complexes has not been finally elucidated, and requires further study[152, 156].

It can be seen from Table 1 that the conductivity of the complexes depends markedly on two factors: the characteristic features of the electronic structure of the metal and the magnitude of the metal–metal distance in the linear conducting chain. Although the dicarbonylacetylacetonato-compounds of iridium and rhodium are isostructural[152] and have identical ligand environments, the conductivity increases by five orders of magnitude on going from the rhodium complex to the iridium complex[151, 152]. This is apparently due to the fact that the outer $5d_{z^2}$ orbitals of iridium overlap more effectively than the outer $4d_{z^2}$ orbitals of rhodium[152] (the overlap in this instance is determined by the size of the *d* orbitals). A similar increase in conductivity is observed on going from palladium complexes to platinum complexes in Magnus' salt and its analogues, and this can also be attributed to the better overlap of the $5d_{z^2}$ orbitals of Pt compared with the $4d_{z^2}$ orbitals of Pd[152, 157]. This correlation is not observed, however, for the dimethylglyoximato-complexes of Ni, Pd, and Pt^{II}; the platinum complex has a lower conductivity than the nickel complex[157]. This may be due to defects in the linear conducting chain; these should have a greater influence on the conductivity in one-dimensional systems than in two- or three-dimensional systems[157].

The influence of the magnitude of the metal–metal distance on the conducting properties is clearly shown by a study of the structure and conductivity of complexes at high pressures (up to 170 kbar)[159]. With increase in pressure to 100–120 kbar, the conductivity of Magnus' green salt and the dicarbonylacetylacetonato-compound of iridium(I) increases sharply (by about 3–5 orders of magnitude)[159]. This is due to a decrease in the distance between the metal ions (by $\sim$ 8–10%) and the corresponding increase in the interaction between them[159, 164]. The p_z and d_{z^2} levels approach one another, the magnitude of the gap decreases, and the conductivity increases. At very high pressures, changes in the metal–ligand distances, which are less sensitive to pressure, begin to have a significant influence on the electronic structure of the complexes. Decrease in these distances has the opposite influence[164]: the p_z and d_{z^2} levels move apart, the magnitude of the gap increases, so that the conductivity should decrease, as is in fact observed experimentally at pressures above 100–120 kbar.

A fairly large number of complexes in which interaction between metal ions with the same valency in a linear chain is assumed have now been prepared[165, 166]. These are chiefly square-planar d^8 complexes of iridium and rhodium with various ligands. Up to the present, however, complexes with a metal–metal distance less than 3.1 Å have not been obtained in this series of compounds.

A second group of electrically conducting complexes containing the complex-forming metal in formally different oxidation states[144] is of considerable interest (Table 2). In these compounds the linear conducting chains are made up of squares with Pt or Ir metal ions at the centres, and

the ligands (CN, CO, etc.) at the corners (Fig. 7). Crystallographically, all the metal atoms in the chain are equivalent, although formally, for example, in the $K_2[Pt(CN)_4]Br_{0.3}\cdot 2.3H_2O$ complex, approximately five out of six platinum atoms are in the bivalent state (Pt^{II}), and one is in the quadrivalent state (Pt^{IV})[144].

Table 2. Electrical conductivity (σ), activation energy (E), and metal–metal distance in various complexes containing linear chains of metal ions in formally different oxidation states.

Complexes	Oxidation state of metal	M–M distance, Å	Refs.	$\sigma_{\parallel}^{a}$ (25°), $\Omega^{-1}\,cm^{-1}$	$E_{\parallel}$, eV	Refs. (conductivity data)
$K_2[Pt(CN)_4]Cl_{0.32}\cdot 2,6H_2O$	+2.32	2.880	160	—	—	—
$K_2[Pt(CN)_4]Br_{0.3}\cdot 2,3H_2O$	+2.30	2.887	160	$(3.5\pm0.5)\cdot10^{2}$[b]	0.07[b]	34, 86, 147
$Mg[Pt(CN)_4]Cl_{0.28}\cdot 7H_2O$	+2.28	2.985	144	—	—	—
$K_{1.74}[Pt(CN)_4]\cdot 1.8H_2O$	+2.26	2.960	144	—	—	—
$Li_{1.64}[Pt(C_2O_4)_2]\cdot 6H_2O$	+2.36	2.81	144	—	—	—
$K_{1.62}[Pt(C_2O_4)_2]\cdot 2H_2O$	+2.38	2.85	144	—	—	—
$K_{1.64}[Pt(C_2O_4)_2]\cdot XH_2O$	+2.36	2.82—2.83[d]	144	0.01—42	0.07—0.086	146
$Mg_{0.82}[Pt(C_2O_4)_2]\cdot 5.3H_2O$	+2.36	2.85	144	—	—	—
$H_{1.6}[Pt(C_2O_4)_2]\cdot 2H_2O$	+2.40	2.80	144	—	—	—
$H_{1.6}[Pt(C_2O_4)_2]\cdot 3H_2O$	+2.40	2.82	144	—	—	—
$Ir(CO)_{2.9}Cl_{1.1}^{e}$	+1.1	2.85	161, 167	0.2	0.064	146

[a] Measured by the four-contact method. [b] $\sigma_{\parallel} : \sigma_{\perp} \sim 200$ (measured by the two-contact method)[147, 162]. [c] $E_{\parallel} \simeq E_{\perp}$. [d] Depending on the water content. [e] $0.95[Ir(CO)_3Cl]\cdot 0.05[Ir(CO)Cl_3]$.

The distances between neighbouring metal atoms are shortened considerably (2.8–2.9 Å), due to the appreciable overlap of the d_{z^2} orbitals (strong metal–metal interaction)[144]. A zone is formed in which the upper levels are only partly filled. Examination of the electronic structure of the complexes has shown that they can be regarded as one-dimensional metals [144, 161].

It was recently shown[34, 86, 146, 147] that compounds of this class have a high conductivity ($\sim 10^2\ \Omega^{-1}cm^{-1}$) along the chain of metal ions ($\sigma_{\parallel}$) (Table 2) and have an activation energy for conduction[34, 86, 146], indicating that these compounds are semiconducting in character[34, 146]. On the other hand, Kuse and Zeller[147], who studied the optical properties of single crystals of the complex $K_2[Pt(CN)_4]Br_{0.3}\cdot 2.3H_2O$ at a frequency of the order of 10^{14} Hz, concluded that the complex is a one-dimensional metal. These authors[147] attributed the activation energy of the conductivity to defects in the linear chain.

An interesting feature is that platinum complexes with mixed valencies are similar in many respects to the highly conducting radical-ion salts of TCQM[34, 86]. They are also characterised by anomalously dielectric constants at a frequency of 10^{10} Hz at liquid helium temperatures[34, 86]. This apparently indicates that highly conducting linear chains exhibit various common features, which are due to the presence of the quasi-one-dimensional electronic system.

Yet another type of highly conducting complex with mixed valencies was discovered recently[168]. Compounds with the compositions $K[Ir_2(CO)_4Cl_4]$ (IX) and $K_2[Ir_2(CO)_4Cl_5]$ (X), in which the iridium atoms are in oxidation states 1 and 2, have been studied[169]. For polycrystalline specimens at room temperature, the conductivity has the values 1.5–5 $\Omega^{-1}cm^{-1}$ and 0.2–0.3 $\Omega^{-1}\,cm^{-1}$ for complexes (IX) and (X) respectively[168]. The activation energy of the conductivity is the same for the two compounds ($\sim$ 0.035 eV). The crystal structure of the complexes is unknown, but it may be expected that the metal ions form a linear chain. The true conductivity of these compounds in a single crystal should be much greater than that found for the polycrystalline specimens.

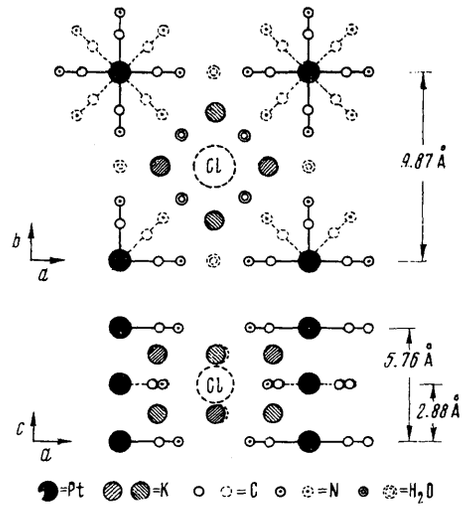


Figure 7. Crystal structure of $K_2[Pt(CN)_4]\ Cl_{0.32}\cdot 2.6H_2O$. Projections along the c and b axes.

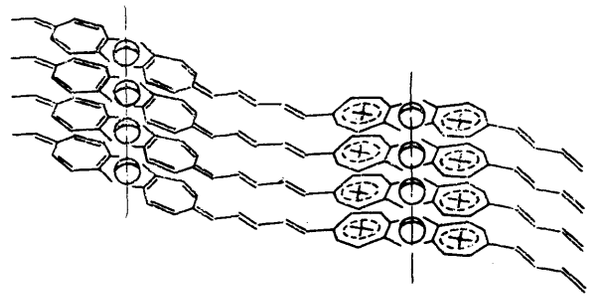


Figure 8. Suggested structure of an exciton superconductor based on metal complexes with readily polarised dyes, containing substituents of the chelate type.

The existence of highly conducting complexes containing linear metallic chains suggests that it may be possible to prepare compounds, based on metal complexes, satisfying the requirements of Little's model[149, 150].

In particular, it is proposed to prepare platinum complexes with mixed valencies, containing a chain of platinum ions and highly polarised ligands[149].

The approaches to the preparation of high-temperature superconductors based on metal complexes have been examined[135]. Various dyes containing substituents of the chelate type have been suggested as starting materials for the preparation of proposed exciton superconductors (Fig. 8). It can be seen from Fig. 8 that the metal ions form linear conducting chains, joining the highly polarised dyes. The preparation of compounds of this type will undoubtedly encounter considerable difficulties associated with solubility, purification, and crystallisation of the products. The intended products may not exhibit the required properties, because of steric complications: non-coplanarity of the dye molecules, non-coplanarity of the carbon atoms of the ring and the ligand atoms, and, which is most important, lack of correspondence between the interplanar spacings for the dyes and the dimensions of the metal atoms.

VI. MODEL OF A TWO-DIMENSIONAL EXCITON SEMICONDUCTOR

In addition to Little's model, the model of a two-dimensional exciton superconductor of the "sandwich" type[3, 4] (Fig. 9), first put forward by Ginzburgh and Kirzhnits[170], is widely known. The conductivity of the "sandwich" is due to a thin metal film ($d \simeq 10-15$ Å), and the attraction between the electrons is increased by the exchange of excitons propagated in the coatings of the "sandwich".

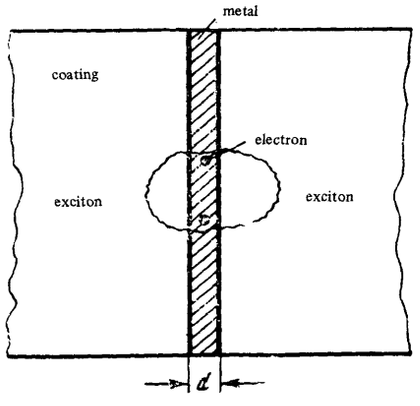


Figure 9. Model of a two-dimensional exciton superconductor of the "sandwich" type: a thin metal film between two coating layers.

The latter may consist of a dielectric, a semiconductor, or even a "poor" metal[3]. The important feature is that electronic excitations (excitons) which are not readily quenched be produced in them. The two-dimensional model of an exciton superconductor has certain advantages over Little's one-dimensional model: the fluctuations of electron density are smaller, and the Coulombic repulsion of the electrons is screened[3]. The interaction between the polarisation and conductivity electrons in the "sandwich" will possibly be weaker[3], however, than that in Little's model. To increase the interaction, the coatings must be very closely joined to the thin metal film (Fig. 9). It seems appropriate to ensure this by chemical interaction between the coating and the film[3]. The existence of chemical binding on the surface of metals has been shown, in particular, in the study of the catalytic properties of metals[171].

The possibility of obtaining high values of T_c in models of the "sandwich" type has stimulated interest in the study of the influence of organic molecules on the critical temperatures of superconducting metal films[176, 177]. The unambiguous interpretation of the changes in T_c observed in studies of this kind[172–177] is fairly complicated, since the critical temperatures of metal films depend markedly on a large number of factors (thickness, nature of the surface, particle size)[177–179]. It should be emphasised that the authors cited were dealing with fairly thick films. In addition to the selection of suitable coatings, the preparation of metal films with thicknesses of several atomic dimensions ($d \simeq 10-15$ Å) presents the main difficulty in the experimental realisation of a superconducting model of the "sandwich" type. Of considerable interest in this connection are granulated superconductors[180], in which fine metal particles are situated in a suitable dielectric matrix. In this instance there is no need to produce a continuous extremely thin metal film.

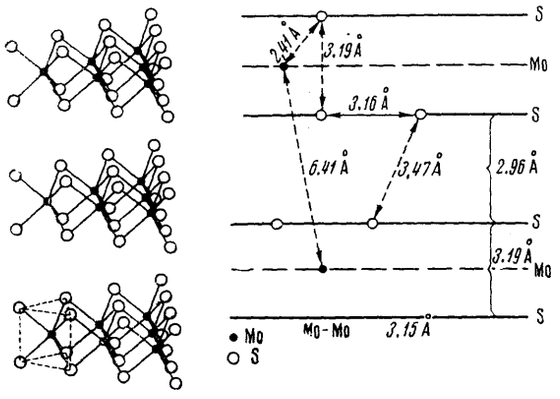


Figure 10. Structure of MoS_2.

In connection with the problem of producing a two-dimensional exciton superconductor, there has recently been an increase in interest in the study of layer compounds. A layer structure is characteristic of many dihalides and dichalcogenides of the transition metals. These include semiconductors, semimetals, metals, and superconductors[181]. Layer compounds of this type can be regarded as consisting of stacks of "sandwiches"[3]. Fig. 10 shows the structure of MoS_2, which is typical of layer dichalcogenides of the transition metals. The layer of molybdenum is situated between two layers of sulphur, and the bonding within this sandwich is strong; the Mo–S distance is equal to 2.4 Å. At the same time, the bonding between the "sandwiches" in the lattice is weak and is determined chiefly by van der Waals' forces; the distance between the sulphur atoms of neighbouring layers is 3.47 Å. The absence of continuous chemical bonding along the c axis

makes it possible to introduce into the transition metal dichalcogenides molecular or atomic layers of various substances: alkali and alkaline earth metals [182], organic bases[183–185], and amides[186]. The introduction takes place between the weakly connected "sandwiches"; the lattice expands along the c axis, with an increase in the distance between the metal layers[182–186]. Graphite, in which the bonding between the carbon layers is weak, is also capable of forming layer compounds of similar type with alkali[186, 187] and transition[188, 189] metals, acids[186], halogens[186], and metal chlorides[186, 189].

Table 3. Superconducting intercalation compounds of TaS_2 with Lewis bases[183, 185].

Bases[a]	pK_a of base	Distance between metal planes	T_c, °K
Pure TaS_2	—	6.04	0.8
$(Pyridine)_{0.5}$	5.3	11.85[b] 12.02	3.55
$(2\text{-Aminopyridine})_{0.53}$	5.2	12.09	3.25
$(2\text{-Dimethylaminopyridine})_{0.32}$		11.94	3.15
$(4\text{-Dimethylaminopyridine})_{0.34}$	9.7	12.25	2.30
$(2\text{-Ethylpyridine})_{0.29}$	6.0	9.64[b] 11.58	3.0
$(3\text{-Ethylpyridine})_{0.29}$	5.7	11.34	4.5
$(4\text{-Ethylpyridine})_{0.33}$	6.0	11.98	2.95
$(2\text{-Isopropylpyridine})_{0.25}$	5.8	11.45	3.80
$(4\text{-Isopropylpyridine})_{0.28}$	6.0	11.98	2.82
$(2\text{-Methylpyridine})_{0.34}$	6.0	11.79	2.95
$(3\text{-Methylpyridine})_{0.33}$	5.7	11.83	2.95
$(4\text{-Methylpyridine})_{0.33}$	6.1	11.76	2.70
$(2,6\text{-Dimethylpyridine})_{0.2}$	6.7	9.59	2.15
$(2,4,6\text{-Trimethylpyridine})_{0.165}$	9.6	9.67	1.95
$(2\text{-Phenylpyridine})_{0.255}$	5.1	11.92	3.15
$(4\text{-Phenylpyridine})_{0.26}$	5.2	12.31	1.6
$(2\text{-Propylpyridine})_{0.245}$	—	11.46	2.85
$(4\text{-Propylpyridine})_{0.25}$	6.1	11.85	2.75
$(Aniline)_{0.75}$	—	18.12	3.06[c]
$(Octadecylamine)_{0.58}$	—	35.02[b] 51.02	3.05[c]

[a]Number of molecules of base per molecule of TaS_2. [b]Two phases. [c]Temperature corresponding to the start of the heat capacity anomalies[185] associated with the conversion into the superconducting state.

Intercalation compounds exhibit interesting properties, particularly electrical[186, 190–195] and magnetic[186, 196, 197] properties. Thus the studies of compounds of graphite with K, Rb, and Cs has shown that these compounds (with the composition C_8M) are converted into the superconducting state at temperatures of 0.55, 0.155, and 0.135° K respectively[191, 192]. Neither the alkali metals nor graphite are superconductors. MoS_2 is a semiconductor[181], but its intercalation compounds with sodium and potassium are "metals"[193], which are converted into the superconducting state at temperatures of ~1.3° K and ~4.5° K respectively[194].

Work on the penetration of strong organic Lewis bases (of the pyridine type) into the superconducting dichalcogenides of Nb, Ta, and Pd is of considerable interest[183–185, 196]. The superconductivity did not disappear, and even a slight increase in T_c was observed (see for example Table 3). By varying the base, it is possible to alter considerably the distances between the metal layers, increasing them to 30 Å or more (Table 3). The ability to form intercalation compounds is here determined chiefly by two factors: 1) the nature of the electronic structure of the original transition metal dichalcogenides, and 2) the characteristic features of the organic Lewis bases, in particular their basic strength and dimensions[183]. Unlike the "metallic" dichalcogenides of Ta and Nb, the "semiconducting" dichalcogenides of Mo and W do not form intercalation compounds with pyridine and its derivatives[183]. TaS_2 forms stable compounds only with bases for which pK_a is greater than 4.[183]

The intercalation compounds obtained show marked anisotropy of the conducting and superconducting properties[185]. The interaction between the layers is weak, and it possibly does not have a decisive influence on the conversion into the superconducting state. There is no correlation between T_c and the magnitude of the distance between the metal planes[184, 185] (Table 3). It is not excluded that the superconductivity in these systems is a property of the two-dimensional metallic layers[187] (two-dimensional superconductivity). These materials are of considerable interest, since their study may provide an answer to the fundamental question of the possible existence of two-dimensional superconductivity. The preparation of intercalation compounds with highly polarised organic molecules appears attractive, and would be of particular interest in connection with the exciton mechanism of superconductivity, which might be produced in systems of this kind.

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The indefinite nature of the theory of the possible existence of high-temperature superconductivity of the exciton type makes it difficult to choose specific chemical routs to the preparation of possible superconducting compounds. The realisation of the models by synthesis in most instances required the development of new approaches and methods.

The results obtained up to the present, however, suggest that it may be possible to obtain compounds with structures corresponding to the existing requirements of theory. In any event, studies of this kind carried out in the field adjoining solid state physics and chemical synthesis will undoubtedly lead to interesting results.

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